CHAPTER 6
ENVIRONMENTAL CHEMISTRY SUBGROUP

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New Jersey Chromium Workgroup Report

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Chromium Environmental Chemistry Subgroup

Summary

There are four main factors that govern the existence, fate, and transport of hexavalent chromium at COPR sites. These four factors are: 1) the nature of COPR, which determines the extent and rate of dissolution from COPR of hexavalent chromium; 2) the hydrodynamics at each site that controls the rate and extent of leaching and transport of hexavalent chromium in soil solution and groundwater; 3) the characteristics of the soil matrix at each site, such as pH and amounts of organic matter and Fe(II) that affect the rate and extent of oxidation and reduction reactions; and 4) the particle size of the various soil types at each site that affects the rate and extent of adsorption of Cr(VI).

COPR contains a number of hexavalent chromium-bearing minerals that were created in a high temperature industrial process. These minerals are otherwise not found in nature and are somewhat unstable over time. The slow dissolution kinetics of the Cr(VI)-bearing minerals in COPR makes it a continuing source of hexavalent chromium to the environment. Given the lack of adequate field or laboratory data to ascertain an appropriate chromium concentration at COPR sites to avoid unacceptable impacts to groundwater, it is necessary to use available scientific tools to predict such an impact. Such tools have been developed as part of NJDEP efforts to propose and adopt soil remediation standards. These Alternative Remediation Standard options were prepared in order to provide expedient procedures for adjusting the generic impact to groundwater clean-up standards to site specific conditions. While these options are applicable to contaminated soil and at some level of COPR-soil mixtures; they are not applicable to the COPR waste material or soil with larger amounts of COPR waste material. Therefore, the Department should consider defining COPR waste material and soil with larger amounts of COPR waste material as a continuing source of contamination to groundwater that will require remediation in accordance with Department's Technical Requirements for Site Remediation (N.J.A.C. 7:26E).

A method is need for distinguishing between continuing source material and COPR-soil mixtures with smaller amounts of COPR where the impact-to-groundwater options are appropriate. However, when circumstances warrant, the Department may allow other procedures for calculating alternative remediation standards. In cases where the groundwater is not currently impacted by overlying chromium waste material, an investigation would be required to determine why such impacts have not been observed, and to demonstrate that conditions at the site will continue to prevent groundwater impacts as long as the source material is present.

Overall, studies in the literature report a wide range of results regarding oxidation of trivalent chromium, Cr(III), to hexavalent chromium, Cr(VI). Research has shown that oxidation can occur in soils, particularly those containing manganese oxides, so it is possible that oxidation takes place in areas where soil has been mixed with the COPR material. Some studies show that

the oxidation reaction is so slow as to be insignificant, while others indicate the oxidation can occur over a period of less than a decade. After much discussion within the group, it appears that there is not a preponderance of evidence in the published literature to warrant a change in the determination of soil clean-up levels based on oxidation reactions. Nevertheless, further study is needed to effectively resolve the issue for COPR sites.

The phenomenon of chromium salts precipitating on surface soils and on structural surfaces, occurring as visible yellow/green blooms, has been documented at the COPR sites in New Jersey where Cr(VI) levels are high. Whether Cr(VI) salts deposit at levels too low to result in visible blooms but high enough to be of an inhalation risk is not known. The subgroup determined that given the complexity of the factors involved, it is difficult at this time to develop a predictive model for this transport mechanism. It is recommended that the Department continue to study the issue through New Jersey-specific research. Regarding the enrichment of Cr(VI) on small, respirable particles, the subgroup found equivocal information. Again, there is not enough data to suggest a change in the application of the generic model, but the subgroup did recommend that ARS petitions submitted for the inhalation pathway provide more detailed information on Cr(VI) concentration by particle size distribution, which can be used in the approval process by DEP.

The Environmental Chemistry subgroup reviewed and discussed these factors within the context of its charges and to make recommendations to the Department. For some aspects of the report, consensus was not possible, as the individuals serving on the work groups were polarized in their professional judgement about some of the issues. This report has attempted to outline those issues for which evidence was presented that demonstrate the theoretical possibility of a phenomenon occurring. However, recommendations have been made only for issues where definitive scientific evidence was presented. The report is intended to serve as an informational resource to the Department and as a foundation for future cleanup decisions at COPR sites in the state to reduce the environmental and public health impacts of chromium contamination. The recommendations are not intended to result in any retroactive application of any new criteria/standards.

Charge Being Addressed

1. Nature of COPR

The interconversion question is imbedded in the larger problem of the nature of chromite ore processing residue (COPR). The physical (micropore) structure of chromite ore processing residue may be the rate-limiting factor in the release of hexavalent chromium. What is the nature of this waste material and how does it influence what we know about chromium chemistry?

Processes that determine the fate and transport of chromium at COPR sites include: 1) continuous dissolution of chromium-containing minerals in COPR; 2) oxidation of trivalent chromium to hexavalent chromium; 3) reduction of hexavalent chromium to the trivalent form; 4) adsorption and desorption of chromium to and from soil constituents; and 5) transport of chromium to groundwater. The fate and transport of chromium at COPR sites is determined primarily by the kinetics that control these processes but modeling these processes is difficult due to the complexity of the variables. Currently, predictions about chromium behavior in this

material are imperfect. Chromium-contaminated soil has properties that are very different from COPR. The focus of this charge is on the nature of the COPR material.

COPR contains a number of hexavalent chromium bearing minerals that were created in a high temperature industrial process. These minerals are otherwise not found in nature and are somewhat unstable over time. The slow dissolution kinetics of the Cr(VI) bearing minerals in COPR makes it a continuing source of hexavalent chromium over decades. Weathering changes the physico-chemical properties of the waste by reducing particle size and increasing the available surface area making it more susceptible for chemical interactions. Treatment and containment strategies for COPR need to take into account the mineralogical characteristics of the waste material. Weathering of COPR subjects the waste to changes in pH, oxidation potential, and ion exchange, all of which may affect the rate and species of chromium being released to the environment. A criteria for distinguishing between pure COPR and COPR-soil mixtures is needed.

In Hudson County, three high-lime chromite ore processing plants operated from around 1905 to 1976 generating 2 to 3 million tons of COPR over the course of their lifetime (Burke et al., 1991). The residual material was produced as a result of extracting chromium from chromite ore. Chromite ore consists primarily of chromium (III), iron, aluminum and magnesium ions in an oxidic matrix. The chromite ore generally used in the manufacturing process contained between 45 to 50% chromic oxide (Cr_2O_3). In the procedure, the ore was crushed and mixed with soda ash and lime and then roasted at 1150 degrees centigrade to oxidize Cr(III) to Cr(VI). Cr(VI) was then extracted from the roast in the form of sodium chromate using a countercurrent water leaching process. The solid residue left after the water extraction is chromate ore processing residue, or COPR. This high alkaline, lime-based roast process, first developed in 1845, was the standard chromate chemical production process used the world over in the first part of the 20th century with only minor differences in the proportion of the mix between the production facilities. The addition of lime resulted in the generation of a highly alkaline COPR. The actual amount of chromium in any COPR is dependent on the efficiency of the chromium extraction process used.

Nature of Chromium at COPR Sites

Chromate chemical production plants around the world have generated millions of tons of chromite ore processing residue from the extraction of chromium from chromite ore. COPR has been used as fill in urban areas in Hudson County, New Jersey and has been disposed of in landfills in Glasgow, Scotland (Geelhoed et al., 2003). The COPR that was used as fill in Hudson County, NJ has a pH of between 11 and 12 and typically contains 3 – 7% chromium present as both Cr(III) and Cr(VI). The two oxidation states of chromium show great contrast in their chemical behavior as well as in toxicity. In the environment, Cr(VI) is present in the anionic form and is relatively soluble and therefore mobile, whereas Cr(III) is virtually immobile and is in general strongly retained in the solid phase.

Weathering of COPR exposes fresh surfaces in the mineral structure. This causes continuous leaching of chromium even decades after it was originally deposited. There is a steady, albeit slow, dissolution of hexavalent chromium from the interior of particles to soils or pore water. This dissolution and subsequent aqueous transport and/or reaction of hexavalent chromium

continues for an unknown period of time (Geelhoed et al., 1999). The actual dissolution rate of chromium from the mineral structure is not known at this time. Farmer et al. (2002) contend that "…site-specific conditions can play an important role in the speciation/fractionazation of dissolved chromium." They attribute the detections of hexavalent chromium in groundwater to the deposition of COPR waste in landfills in Scotland, which occurred from 1803 to 1968. They also found that reduction of Cr(VI) to Cr(III) occurred significantly presumably due to the presence of high levels of organic matter present at the sites.

Researchers from the Macaulay Institute and the University of Edinburgh in Scotland used a range of analytical techniques including scanning electron microscopy, x-ray powder diffraction and x-ray fluorescence spectrometry to characterize COPR material deposited at three sites in Scotland (Hillier et al., 2003). An integrated analytical and experimental approach using both solid and solution–phase techniques has enabled researchers to identify the Cr(VI) substituted minerals involved in the slow release of Cr(VI) from COPR (Geelhoed et al., 2002). Equilibrium modeling indicated that, at pHs greater than 11 (typical of the Scottish COPR sites), concentrations of Cr(VI) in solution were controlled by the high-temperature minerals Cr(VI)-substituted hydrogarnet and Cr(VI)-hydrocalumite, a layered double-hydroxide clay with chromate ions held in the interlayers. These phases dissolved below pH 11, resulting in a sharp increase in predicted Cr(VI) concentrations in solution. At pH 9.5-11, agreement between results of batch dissolution experiments (conducted over 4 and 26 days) and model predictions of Cr(VI) in solution was improved by addition of Cr(VI)-ettringite (a secondary phase precipitated when hydrocalumite dissolves) to the model. COPR chemistry is dominated by calcium aluminate phases; although pH was a significant variable in predicting release of Cr(VI) from the COPR minerals, the buffering capacity of the COPR material is large. Consequently, large pH changes in the field were considered unlikely by the researchers. The model overestimated the buffering capacity of the COPR system at lower pHs (9.5 and 10.5), compared with experimental results, which the researchers attribute to "the relatively slow dissolution kinetics of the various phases in COPR."

Gradations of material containing COPR waste material mixed with soil or mixed with other material may behave differently from either COPR alone or soil. For example, impact to groundwater models appropriate for COPR-soil mixtures may not be appropriate for pure COPR slag. Therefore, it is important that pure COPR and COPR-soil mixtures be accurately defined and differentiated. At a later date, the soil standards committee should convene a group to establish guidelines that distinguish between COPR and COPR-soil mixtures. Factors such as pH, reducing conditions, mineralogy etc. are candidate factors to use in making the distinctions.

Charge Being addressed

2. Transport to Groundwater:

What concentration of chromium in the soil at the chromite ore processing residue sites results in chromium levels above the drinking water standard in groundwater? Do the NJDEP clean-up standards currently under development adequately protect groundwater?

This charge was divided into two principal components based upon the two questions in the charge.

a. What concentration of chromium in the soil at the chromite ore processing residue sites results in chromium levels above the drinking water standard in groundwater?

Laboratory studies have confirmed field observations that hexavalent chromium (Cr(VI)) is readily leachable from chromite ore processing residue (COPR) waste material and may result in groundwater concentrations that exceed the New Jersey groundwater quality criteria.

Geelhoed et al. (2002) tested the leaching potential of COPR waste from Scotland. The total chromium concentration was approximately 40,000 mg/kg (via x-ray fluorescence), with about 30% of this in the hexavalent form (determined using x-ray absorption near-edge structure spectroscopy). In batch leaching experiments (4 or 26 days in duration and across a range of pH values), measured aqueous chromium concentrations ranged from 46,000 to 750,000 µg/L, with the highest concentration at pH 8 (liquid to solid ratios of 10:1 or 5:1). These concentrations are well above the NJDEP groundwater quality criterion of 100 µg/L for chromium, and indicate that from 0.5 to 9 percent of the total chromium was removed by the batch leaching test, or 2 to 30 percent of the hexavalent chromium. Above pH 10.5, concentrations appeared to be controlled by the solubility limit of hexavalent chromium-containing minerals (discussed below). Between pH 8 and 10.5, concentrations were higher but did not appear to reach equilibrium due to slow dissolution kinetics. Below pH 8, chromate concentrations decreased due to adsorption of the dissolved chromate on freshly precipitated aluminum and iron hydroxides. Thus, the actual mechanism controlling chromate concentrations in solution was pH dependent.

Weng et al. (1994) investigated the leachability of COPR waste from Liberty State Park in Hudson County, New Jersey using batch studies and found a smaller pH dependence on the resulting chromium concentration in the leachate. Untreated COPR contained total chromium concentrations of approximately 50,000 mg/kg using scanning electron microscopy x-ray energy dispersion analysis, or 25,000 using hydrofluoric acid digestion. Aqueous concentrations of chromium in batch leaching experiments ranged approximately from 100 to 1,500 µg/L, which are likely to be lower than field conditions because of the large volume of extractant employed (liquid to solid ratio of 200:1). However, these concentrations were again at or above the New Jersey groundwater quality criterion, and chromium removed by the batch leaching test range up to 1% of the total chromium amount. The amount of organic matter was found to influence the concentration in the leachate, in that reduction of Cr(VI) was apparent in the presence of organic matter. In a more realistic simulation of leaching processes in the field, Weng et al. (2002) conducted column leaching studies using the same Hudson County waste material. Chromium concentrations in the column eluate over the first two days of leaching (about 25 pore volumes) ranged from 1,000 – 70,000 µg/L. Again, about 1% of the total chromium was readily leachable.

James (1994) studied the leachability of COPR waste from Hudson County and suggested that the soluble chromium was controlled by dissolution of chromate salts. He tested material with both high (10,400 mg/kg) and low (1,800 mg/kg) total chromium concentrations (determined using hydrofluoric acid digestion), and found that under mild extraction conditions, about 2.5% of this amount was readily leachable hexavalent chromium. This was found to be about half the

amount of hexavalent chromium determined using the USEPA modified alkaline digestion Method 3060 (USEPA 1982).

The above studies indicate that a few percent of the total chromium in COPR waste material is in the readily leachable hexavalent form and may result in concentrations in the leachate that exceed the groundwater quality criteria for this metal. Thus, there is a concern that groundwater may become contaminated from leaching of chromium from overlying waste. However, systematic laboratory studies correlating total chromium concentrations with particular chromate concentrations in the leachate have not been reported. Such studies could be conducted; however, recent evidence from NJDEP procedures for assessing dermal exposures to chromium suggests that such a correlation may be poor (NJDEP 2004a).

Field observations at COPR sites have yielded the full range of possible outcomes pertaining to groundwater impacts from overlying chromium contamination. COPR contaminated sites can be categorized by the volume of contaminant present, the concentration and speciation of the contaminant, the distance of the contaminant to groundwater, and whether or not there are unique physical characteristics present that would impact the behavior of the discharge. These unique physical features would include the presence of a sewer line, meadow mat, high organic content soils, existing impermeable surfaces, etc.

A preliminary survey of 40 sites under the jurisdiction of Tierra Solutions, Inc., is illustrative. Seventeen of these sites have large amounts of COPR material in or at the water table and have elevated levels of hexavalent chromium in the groundwater. The remaining sites showed no elevated chromium levels in the groundwater. These sites either have low levels of chromium contamination or have high levels of chromium 2-7 feet above the water table. Most of the Honeywell (Allied-Signal) sites have large amounts of COPR deposited, often extending into the water table, and most exhibit some level of groundwater contamination. In contrast, only two of thirteen sites known as Orphan I sites exhibit groundwater contamination above the Groundwater Quality Standards. These sites have low levels of chromate waste. Half of the twenty-four July 93 Directive Chrome sites have groundwater contamination.

Some of the cases discussed above with high levels of contamination do not yet exhibit contaminated groundwater, despite the length of time COPR material has been present. Some of these cases involve only a short transport distance between the source of contamination and the water table. The lack of groundwater impact in these cases could be attributed to 1) reduction of hexavalent chromium during transport between the source and the water table, 2) high adsorption of hexavalent chromium to the unsaturated zone waste material or soil, or 3) an incomplete transport pathway because of the lack of a hydrological connection between the chromium source and the aquifer under observation.

The potential for reduction of hexavalent chromium reduction in soils has been discussed by several researchers (Bartlett and James 1988, Zayed and Terry 2003, Losi et al. 1994, Wittbrodt and Palmer 1995, Jardine et al. 1999, Kozuh et al. 2000). Reduction is thought to occur in the presence of soil organic matter and Fe^{2+}, and evidence for partial reduction of chromium in COPR material has been observed as well (Weng et al. 1994, James 1994). In France, limited migration potential of hexavalent chromium in groundwater contaminated by COPR material

was observed due to likely reduction by ferrous iron (Loyaux-Lawniczak et al. 2001). Several of the New Jersey chromium sites contain meadow mats that lie at or near the water table which appear to either reduce or adsorb hexavalent chromium, such that significant chromium impacts to the groundwater have yet to be observed. However, it is difficult to predict whether this mechanism will operate indefinitely. Given a continuing source of fresh hexavalent chromium leachate from continued dissolution/oxidation of the overlying waste material, the reduction capacity of the available reducing agents (the meadow mat in this case) could ultimately be exceeded. Then, breakthrough of hexavalent chromium material to the groundwater might be observed.

Renewal of reducing agents may slow the rate at which their reducing capacity is exhausted. In particular, the Fe(III) produced by reduction of Cr(VI) can be reduced again to Fe(II) by humic and fulvic acids, and be available for another cycle of reducing CR(VI). Wittbrodt and Palmer (1996) pointed out that differing rates for redox reactions (Fe(III) reduced by organic matter; Cr(VI) reduced by organic matter; Cr(VI) reduced by Fe(II)) can allow for redox cycling of iron in the system organic C-Fe-Cr. Wielinga et al. (2001) describe a role for dissimilatory iron-reducing bacteria in this process, whereby Fe(III) is reduced in microbial respiration and acts as an electron shuttle, catalyzing the reduction of Cr(VI). Depending upon the chemical environment, iron can be cycled more than once.

In cases where chromium reduction occurs during groundwater transport, the plume length may slowly increase as reducing agents in the aquifer material are consumed. Whether or not breakthrough or plume lengthening would actually occur would require quantitative knowledge of the reduction capacity of the reducing agent, whether redox cycling of iron is occurring, the total amount of hexavalent chromium that would ultimately pass through this organic material, and whether the kinetics of this reduction process would continue to be adequate as the reducing agent was depleted. While at least one investigator is looking into methods for assessing reduction capacity of naturally occurring reducing agents (Lee and Batchelor 2003), much additional research is needed before it will be possible to ascertain the ultimate impact of chromate waste sites on soil and groundwater. Thus, it is difficult to predict whether COPR sites that do not exhibit chromium-contaminated groundwater at the present time will continue to do so as hexavalent chromium continues to leach in future decades.

Turning to the issue of adsorption/desorption of hexavalent chromium, some quantitative information is available pertaining to its adsorption to soil (as opposed to COPR waste) that enables a limited assessment of its potential to impact groundwater. Although hexavalent chromium is frequently considered to be a relatively mobile contaminant, this assessment may be influenced more by the observation that it is readily released from waste material, rather than actual observed transport rates through soil. While this metal is relatively mobile relative to certain other metallic contaminants, such as lead or trivalent chromium, it is nonetheless retained by soil to a significantly greater extent than water-soluble anions such as chloride and nitrate, which generally transport readily through the soil. Soil adsorption coefficient values for hexavalent chromium reported in the USEPA Soil Screening Guidance Document range from 1 to 1,800 L/kg (USEPA 1996). NJDEP studies relating to assessing the dermal exposure pathway also suggest a wide variation in values (NJDEP 2004a). Direct measurement of soil adsorption coefficients on twelve New Jersey soils using freshly applied chromate salts yielded adsorption coefficients ranging from about 3-13 L/kg (Allen et al. 1994, NJDEP 2004b). This latter range

of adsorption coefficients, when used in the SESOIL unsaturated zone transport model (Bonazountas and Wagner 1984), indicate that the time for hexavalent chromium to transport 10 feet downward through sandy loam soil ranges from 6 to 70 years (NJDEP 2004c). However, even in cases where it might appear that hexavalent chromium is highly adsorbed to soil, there may still be a concern for potential groundwater impacts. A continuing source of fresh hexavalent chromate leachate from overlying COPR material may eventually saturate all soil adsorption sites in the soil column, at which time rapid breakthrough of chromium to the water table might be expected.

If some COPR sites show a lack of a groundwater impact because of a lack of a hydraulic connection between the waste material and the groundwater, the transport pathway is incomplete and need not be evaluated. However, the lack of such a connection should be demonstrated and consideration should be given to where infiltrating water is being routed. Another receptor may be of concern. In addition, if the site is disturbed due to construction or other activities, the lack of a hydraulic connection would have to be reconfirmed.

To summarize, various concentrations of COPR or chromium-contaminated soil have been indicated to be a threat to groundwater quality, while similar concentrations in other situations have not impacted groundwater. The minimum concentration of chromium at COPR sites that may result in an unacceptable groundwater impact is unknown at the present time and is certain to be site-specific. Furthermore, direct measurement of chromium concentrations in the groundwater indicate current conditions, but do not necessarily predict possible future impacts to groundwater. Thus, laboratory and field data are inadequate to answer the first charge regarding a definitive concentration of chromium at COPR sites that result in contamination of groundwater above the chromium Groundwater Quality Criterion.

Given the lack of adequate field or laboratory data to ascertain an appropriate chromium concentration at COPR sites to avoid unacceptable impacts to groundwater, it is necessary to use available scientific tools to predict such an impact. Such tools have been developed as part of NJDEP efforts to propose and adopt soil remediation standards. This then leads to a discussion of the second charge:

b. Do the proposed soil clean-up standards adequately protect groundwater?

The NJDEP has not yet proposed soil clean-up standards. However, it is planning to propose soil clean-up standards that include generic soil standards and site-specific options for protection of groundwater from leaching of contaminants from soil (NJDEP 2004d). The purpose of the Impact to Groundwater Soil Remediation Standards is to prevent the unacceptable risk to human health from the ingestion of contaminated groundwater, caused by the migration of chemicals from the unsaturated soil zone to the groundwater. While these standards and procedures may be suitable for chromium-contaminated <u>soil</u>, their applicability at COPR sites is limited due to the unusual nature of the source contamination.

For this reason, chromium has been removed from the list of contaminants that will be included in the proposal, and is separately discussed here. The following discussion consists of seven sections:

1) a discussion of the USEPA methodology for calculating generic impact to groundwater soil clean-up standards,
2) a discussion of why this methodology is unsuitable for COPR sites,
3) an assessment of the applicability of alternate options for calculating impact to groundwater soil cleanup standards at COPR sites,
4) the recommended approach for managing COPR material,
5) the recommended approach for managing chromium-contaminated soil,
6) distinguishing COPR material from chromium-contaminated soil, and
7) Other Alternative Remediation Standard Procedures ("Tier III Standards")

1) USEPA Methodology for Developing Generic Impact to Groundwater Remediation Standards

The USEPA Soil Screening Level (SSL) Guidance Document (USEPA, 1996) recommends the use of the simple partitioning equation to calculate inorganic soil cleanup standards for the Impact to Groundwater Pathway (USEPA, 1996, Equation 22):

$$IGWSRS = C_{gw}\left\{(K_d) + \frac{\theta_w + \theta_a H'}{\rho_b}\right\}DAF \qquad \text{Equation (1)}$$

where:

$IGWSRS$ = Impact-to-groundwater soil remediation standard (mg/kg)
Cgw = Health Based New Jersey Groundwater Quality Criteria (mg/L)
Kd = soil-water partition coefficient (L/kg)
θ_w = water-filled soil porosity (L_{water}/L_{soil})
θ_a = air-filled soil porosity (L_{air}/L_{soil})
H' = Henry's law constant (dimensionless)
ρ_b = dry soil bulk density (kg/L) = 1.5 kg/L
DAF = dilution-attenuation factor

For New Jersey purposes, Equation 1 is expanded to separate the target leachate concentration discussed in the USEPA document into its component parts. The target leachate concentration is the product of the groundwater criteria (C_{gw}), and the dilution-attenuation factor (DAF). This modification allows the New Jersey groundwater quality criterion to be directly entered as an input parameter. The DAF is calculated via Equation 2. This equation requires a value for the mixing zone depth in the aquifer, which is calculated using Equation 3. These two equations are taken from USEPA SSL Guidance Document (USEPA, 1996, Equations 37 and 45), respectively.

Equation for calculating the dilution-attenuation factor (DAF):

$$DAF = 1 + \frac{Kid}{IL}$$

Equation (2)

Where:
i = gradient (m/m)
d = mixing zone depth (m), calculated below (Equation 3)
I = infiltration rate (m/yr)
L = length of area of concern parallel to groundwater flow (m)
K = aquifer hydraulic conductivity (m/yr)

Equation for calculating the aquifer mixing zone depth, d:

$$d = (0.0112L^2)^{0.5} + d_a\{1 - \exp[(-LI)/(Kid_a)]\}$$

Equation (3)

Where:
d_a = aquifer thickness (m)

This equation assumes that contaminants in soil exist in equilibrium between the sorbed phase (on soil solids), aqueous phase (in soil moisture) and vapor phase (in the soil airspace). The equations calculate the total amount of the contaminant that may be left behind in the soil such that the aqueous phase concentration of the contaminant will not exceed a specified criterion. The criteria for New Jersey are the health-based groundwater quality criteria. Since soil water will actually be diluted once it enters the groundwater, a dilution-attenuation factor (DAF) is included in the equation to account for this process. Dilution of the contaminant due to transport through the unsaturated soil zone is not included; the chemical in soil is assumed to be immediately adjacent to the water table. Chemical degradation is also not included in this model; the calculations assume that groundwater quality must be achieved immediately after remediation.

2) USEPA Methodology not suitable for COPR waste sites

The USEPA simple partitioning equation assumes that contaminant concentrations in soil solution is controlled by <u>adsorption-desorption</u> equilibrium processes, as quantified by the soil-water partition coefficient (K_d). This model may useful for chromium contamination in <u>soil</u>. In contrast, COPR waste sites may consist of pure slag waste material, chromium-contaminated soil, or a mixture of both. COPR slag waste material is not soil and exhibits fundamentally different properties than contaminated soil. Available evidence indicates that the leachable chromium in COPR slag waste results from <u>dissolution</u> of hexavalent chromium-containing

minerals in the waste residue, rather than adsorption-desorption between the solid and solution phases (James, 1994; Geelhoed et al. 1999; Hillier et al. 2003; Geelhoed et al. 2002). Specific hexavalent chromium containing minerals implicated in this dissolution process are hydrocalumite, hydrogarnet, and ettringite, which appear to be formed during chromite ore processing or COPR weathering. There is also a possible presence of calcium chromate, although this has not been regularly observed (Moerman 1996).

The concentration of chromium in soil solution resulting from dissolution would be controlled by the solubility of the chromium minerals, the kinetics of the dissolution process, and the effects of slag constituents on the solubilization process. This is an entirely different mechanism from the simple partitioning equation.

The dissolution process of a mineral may be described as:

$$AB(solid) \leftrightarrow A^+(aq) + B^-(aq)$$
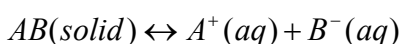
Where AB represents the undissolved solid mineral, and A^+ and B^- represent the cation and anion in solution. As shown, the reaction will eventually proceed to equilibrium, and dissolution and precipitation reactions will be equal. At equilibrium, the solution phase is said to be <u>saturated</u> with the salt (mineral) of interest. This may be quantitatively expressed as:

$$K_{sp} = [A^+] \times [B^-]$$

where K_{sp} is the solubility product (units dependant on the salt) and $[A^+]$ and $[B^-]$ represent the concentrations of the cation and anion at saturation.

A fundamental difference between this process and the adsorption-desorption process is that the concentrations of the constituents in solution after dissolution are independent of the concentration of the mineral in the solid phase, so long as that mineral is still present at mineral solubility equilibrium. This appears to be the case at the chromium waste sites, since solid mineral continues to be present to generate hexavalent chromium. In contrast, the simple partitioning equation (adsorption-desorption model) assumes a <u>linear relationship</u> between the sorbed phase concentration and the solution phase concentration. Thus, the two models are not compatible and the USEPA partitioning equation is not appropriate for use with COPR waste material. While the use of the K_d parameter as an empirical, rather than theoretical, parameter might prove useful in assessment of hexavalent chromium leaching from COPR waste, an evaluation of this possibility has not been conducted at the present time.

For portions of a chromium waste site that consist of chromium-contaminated <u>soil</u>, or a mixture of COPR waste and soil, the simple partitioning model is theoretically applicable, since the solid phase contains components that participate in adsorption-desorption processes. However, the use of this model for inorganic contaminants is complicated by the presence of multiple oxidation states of chromium and the presence of various chromium complexes, each of which would have a different K_d value. Furthermore, the K_d values are dependant on soil pH. Finally, when chromium-contaminated soil is subjected to continued sources of hexavalent chromium from adjacent or overlying COPR source material, the chromium-adsorbing sites on the soil may

eventually become saturated, under which conditions the simple partitioning equation would no longer apply. Therefore, the NJDEP has decided that generic use of the simple partitioning model is not suitable for determining impact to groundwater soil cleanup standards for COPR waste sites.

Assessment of the potential of using a generic dissolution model to determine a generic impact to groundwater soil cleanup standard at COPR waste sites

It is of interest to explore the possibility of using a dissolution model to determine a generic impact to groundwater standard for COPR material. The solubility model indicates a <u>constant</u> aqueous concentration of hexavalent chromium would be observed in solution at equilibrium (so long as adequate solid phase is present) regardless of the chromium concentration in soil. This aqueous concentration will either be above or below the chromium criterion in groundwater. With this model, the leachable concentration of chromium in COPR waste does not necessarily correlate with the total concentration in the solid phase, and calculation of an acceptable soil concentration for protection of groundwater is problematic.

Laboratory studies of COPR waste material, on the other hand, indicate that leachate concentrations of hexavalent chromium are sensitive to pH, the soil-to-water ratio used, and the time of leaching or extraction. This implies that 1) pH affects concentrations of other COPR constituents in solution, which in turn, affect chromate concentrations, and 2) the dissolution reactions frequently do not proceed to equilibrium (i.e. saturation).

Relating to the pH effect, the solubility of minerals in solution is more complex than the simple model described in the previous section. Different salts containing common ions (sulfate, chromate, carbonate, calcium, etc.) will interact with each other and influence the concentration of each species in aqueous solution. The pH (concentration of hydrogen ion in solution) also affects a species solubility behavior. This is known as the common ion effect, and determining the equilibrium concentration of each species in solution requires a knowledge of all minerals (salts) present in the solid phase, and the solubility products for each. Then, the concentration of each species is calculated by assuming simultaneous equilibria of all species. This requires advanced modeling using models that calculate the various simultaneous equilibria, such as the MINTEQ model (Allison et al 1991). Such models are advanced research models not suitable for routine regulatory use.

To elaborate on the second statement (non-attainment of dissolution equilibrium), Geelhoed et al (2002). presented evidence that between pH 10 and 12, dissolution of chromate minerals in batch leaching experiments proceeded to equilibrium in 24 hours, while at lower pH values, equilibrium was not attained due to slow dissolution kinetics, even though the observed leachate concentration was higher at the lower pH values. Under field conditions, it is even less likely that chromium concentrations will reach saturation levels during storm events, or during soil moisture infiltration.

The simple dissolution model described above is therefore inadequate to describe either laboratory experiments or field observations. Given the insufficient understanding of the various factors controlling the dissolution process, an alternate generic model for calculating generic

impact to groundwater clean-up standards based on the dissolution process is not available at this time.

3) Assessment of the use of Alternative Remediation Standard Procedures at COPR sites

NJDEP plans to propose several procedures that allow for the calculation of site-specific alternative remediation standards for the impact to groundwater pathway. Six options have been described in the draft proposal (NJDEP 2004d). They are briefly outlined below, but most are not applicable to COPR material as they often require assumptions incorporated in the simple partitioning model discussed above. For more details on these options, see NJDEP 2004d.

 Option A. Site-Specific modification of the simple partitioning equation

As discussed above, the simple partitioning equation was judged to be unacceptable for calculation of generic chromium impact to groundwater soil clean-up standards at COPR waste sites, and it may not be used for COPR slag waste material. However, it may appropriate for use with chromium-contaminated <u>soil</u> if a site-specific K_d value is available. A site-specific K_d value may be determined for chromium-contaminated soil using the Synthetic Precipitation Leaching test (see Option C below). Additionally, a site-specific dilution-attenuation factor (DAF) may be calculated from knowledge of the infiltration rate and/or aquifer properties.

Option B. Immobile chemicals

This option essentially results in a waiver for the impact to groundwater pathway for chemicals that are highly adsorbed to soil and are located a minimum of two feet above the water table. As discussed in the basis and background document, these chemicals are never expected to reach the water table. Chromium sites are not eligible for this option since hexavalent chromium is a relatively mobile contaminant (USEPA 1996).

Option C. Synthetic Precipitation Leaching Procedure

This procedure is a standard USEPA test method (USEPA Method 1312) that directly measures the leaching potential of contaminants from contaminated soil and waste material. The draft proposed soil standards basis and background document describes several approaches for interpreting the results of this test, including pass/fail options and options for calculating site-specific alternative remediation standards. Some of them require calculations that use the simple partitioning model and are unsuitable for use with COPR material, but may be used with chromium-contaminated soil. Other options make no assumptions regarding the nature of the leaching process and are therefore generally acceptable for use. Given the facile leaching of hexavalent chromium from COPR slag waste sites, it is likely that many of these samples will not pass the leaching test. The use of this option with chromium-contaminated <u>soil</u> may be more useful.

Option D. SESOIL transport modeling when groundwater has not yet been impacted

This option allows the use of SESOIL, a vadose zone contaminant transport model (Bonazountas and Wagner 1984), to estimate the impact to groundwater of soil contaminants. The simulation model uses soil, chemical, environmental, and meteorological inputs to determine this impact. SESOIL is unsuitable for use with COPR slag waste material because it assumes an adsorption-desorption mechanism for soil contaminants. However, it may be useful with chromium-contaminated soil if a site-specific Kd value is available.

Option E. Vadose Zone/Groundwater Modeling (SESOIL/AT123D)

This option is used where groundwater has already been impacted by a contaminant. It allows a combination of vadose zone and groundwater transport modeling to demonstrate contaminant concentrations in the groundwater will achieve compliance with the groundwater quality criteria within a specified time frame. It is not appropriate for COPR waste material due to the same limitations described in Option D, but may be useful for chromium-contaminated soil.

Option F. Consideration of Observed Groundwater Conditions

This option essentially allows for a waiver for cases where contamination is in direct contact with the water table and no groundwater impacts are observed. This situation may occur for highly adsorbed contaminants, or in the case of COPR sites, where dissolution of the contaminant is slow enough that chromium concentrations in groundwater do not exceed 100 µg/L. To qualify for this option, the highest contaminant concentrations observed at the site must be present at the water table. Further details on the application of this option are described in the proposed soil standards impact to groundwater basis and background document.

4) Recommended approach for managing the impact to groundwater of COPR waste material: treatment of COPR material as contaminant source

Of the six options for calculation of Alternative Remediation standards discussed above, only Option F, and to a limited extent, Option C, are suitable for use with COPR waste material. However, as explained above, NJDEP anticipates that the results of Option C will indicate that all concentrations of chromium typically associated with COPR slag waste material are unacceptable. Furthermore, it is anticipated that Option F will never be useful when COPR material is present at the water table, because groundwater impacts in these cases will typically be above the groundwater quality criteria. Because of these issues, the leachability of hexavalent chromium from COPR material, and the inappropriateness of both the generic impact-to-groundwater simple partitioning equation, the NJDEP has decided to treat COPR waste material as a continuing source that will require remediation in accordance with the Technical Requirements for Site Remediation (N.J.A.C. 7:26E) for protection of groundwater.

By treating the COPR material as a continuing contaminant source, it falls outside the scope of the impact to groundwater soil clean-up standards, which pertain to calculation of clean-up standards for contaminated soil.

5) Recommended approach for managing chromium-contaminated soil

As opposed to COPR material, chromium-contaminated <u>soil</u> falls under the scope of the impact to groundwater soil clean-up standards, because the models and assumptions contained in the standards are appropriate.   While the Department feels that the generic use of the simple partitioning equation for chromium-contaminated soil is inappropriate, all six options for calculating an Alternative Remediation Standard may be used, so long as overlying COPR material has been remediated in accordance with N.J.A.C. 7:26E requirements to prevent any further or future impacts to groundwater. The reason for this restriction is that a continuing source of fresh hexavalent chromate leachate from overlying COPR material may eventually saturate all soil adsorption sites in the soil column, at which time the simple partitioning model no longer applies and rapid breakthrough of chromium to the water table might be expected.

6) Distinguishing COPR from chromium-contaminated soil

Many areas at chrome waste sites consist of a mixture of chromium-contaminated soil and COPR material. The most conservative way to treat these mixtures would be to treat all material that contains any COPR residue as source material. However, this ignores the ability for waste material containing substantial amounts of soil to behave as chromium-contaminated <u>soil</u>, in that hexavalent chromium dissolving from COPR minerals may participate in the adsorption-desorption mechanisms on soil particles that are also present. On the other hand, material containing mostly COPR material and only small amounts of soil probably behaves similar to pure COPR waste material, in that the small amount of soil present may become saturated with the high concentrations of chromium leaching from the source material and no longer adsorb chromium. A reasonable strategy is therefore proposed where material consisting largely of COPR be treated as source material, and material that consists largely of contaminated soil can be treated using the soil clean-up standard guidelines. In the field, a mechanism for separating out these two classifications is needed. While various strategies should be investigated, it is suggested that pH measurements may be a practical means for accomplishing this task. The pH of New Jersey soils typically range from about pH 4 to pH 6.5 (Lee et al. 1996, Yin et al. 1996), while pure COPR source material typically ranges from pH 10-12. Both the COPR and soil have high buffering capacities, and it is reasonable to expect that mixtures of the two materials would exhibit pH values between 6.5 and 10. A value within this range is suggested as a decision point when classifying the tested material. Further investigation should be conducted to determine a suitable pH. Material exhibiting pH values less than this value may be treated as chromium-contaminated soil. Material with a pH above this level will be treated as source material.

It has also been observed that pure COPR material typically exhibits higher chromium concentrations than chromium-contaminated soil impacted by the source material. This suggests another potential method for classifying the waste material could involve chromium concentration criteria. However, a suitable concentration criterion is not available at the present time.

NJDEP recognizes that the mixture of COPR and soil is a particularly complex issue because it is unclear how to best identify COPR and the extent of its influence over the soil matrix. In addition to the above suggestions, a weight of evidence approach may be appropriate. Research is recommended to sort out the various options available.

7) Other Alternative Remediation Standard Procedures ("Tier III Standards")

As described in the Brownfield and Contaminated Site Remediation Act, the Department is required to consider site-specific adjustments to the generic soil remediation standard:

58:10B-12f.(1) *A person performing a remediation of contaminated real property, in lieu of using the established minimum soil remediation standard for either residential use or nonresidential use adopted by the department pursuant to subsection c. of this section, may submit to the department a request to use an alternative residential use or nonresidential use soil remediation standard. The use of an alternative soil remediation standard shall be based upon site-specific factors which may include (1) physical site characteristics which may vary from those used by the department in the development of the soil remediation standards adopted pursuant to this section… and physical characteristics of the site, including, but not limited to, climatic conditions and topographic conditions.*

For this reason, the Alternative Remediation Standard options discussed above were prepared in order to provide expedient procedures for adjusting the generic impact to groundwater clean-up standards to site specific conditions. These options are ones that the department felt would be regularly useful, and are therefore specifically described. However, when circumstances warrant, the Department may allow other procedures for calculating alternative remediation standards. These procedures will be reviewed on a site-specific basis, and will require substantially more time for review than the predefined alternative remediation standards discussed above. The field data collected may be considerably greater than that normally acquired during site investigation. Additionally, the proposed approach may involve alternative or more advanced models than those proposed by the NJDEP. In other words, effort required for these "Tier III" procedures will be substantial greater than a routine investigation of the site, and approval of such procedures shall require adequate support from the published scientific literature. NJDEP wishes to emphasize, that for reasons discussed above, the determination of current groundwater conditions at a particular site is not adequate to elucidate potential future groundwater impacts at the site. In cases where the groundwater is not currently impacted by overlying chromium waste material, an advanced investigation would be required to determine why such impacts have not been observed, and to demonstrate that conditions at the site will continue to prevent groundwater impacts as long as the source material is present.

Charge Being Addressed

3. Interconversion

What is the capacity of trivalent chromium to convert to hexavalent chromium in the soil of the chromate ore processing residue sites? Do the current remediation standards adequately account for this interconversion? If not, recommend some options the Department should pursue to address any discrepancy or inadequacy, including research.

The general conclusion from all of the literature reviewed so far is that the factors controlling oxidation of Cr(III) to Cr(VI) are numerous but relatively defined. Determining the dominant

variable at a specific site is more complex, in particular because sites containing COPR vary in the proportions of COPR material to soil.

Fantoni et al. (2002) studied the oxidation of Cr(III) to Cr(IV) released from serpentinized ultramafic rock (ophiolites) in Italy. These researchers speculate that the release of chromium from these Cr-rich rocks to groundwater "requires oxidation of Cr(III) to Cr(VI)"; manganese oxides, hydrogen peroxide, gaseous oxygen and Fe(III) oxyhydroxides are considered likely electron acceptors. The pH of the groundwater in the area was reported to be 7.6. Likewise, Oze et al. (2004) observed that, although ultramafic rocks collected from New Caledonia, Oregon and California contain Cr(III) exclusively, Cr(VI) was identified in the soil solutions. They attribute this to some oxidation of Cr(III) in Cr-spinels by high-valent Mn oxides. Thus, both studies state that some oxidation of the natural Cr(III) is occurring in these systems. Cooper (2002) reports that oxidation of Cr(III) to Cr(VI) due to Mn(III/IV) oxides caused chromium toxicity in Zimbabwean ultramafic soils (pH about 6). The toxicity/oxidation in formerly wetted Fe-Mn concretionary subsoils occurred after 8 years of air-dry storage. Toxicity due to oxidation also occurred in well-aerated soils treated with $KMnO_4$. This researcher cites work by Silvester et al. (1995) indicating that oxidation is possible only in the aqueous phase. Cooper (2002) indicates that labile Cr(III) that can be oxidized is likely to be present in clay-rich ultramafic soils, and that oxidation "is probably continuous in concretionary subsoils subject to wetting-drying cycles."

Most researchers agree that Cr(III) oxidation can occur in various media if the appropriate manganese oxides are present and if other conditions are also favorable. Not only pH, but oxygen, sunlight, organic matter, and Fe-oxides may affect chromium redox reactions, as may the phase containing Cr(III). James (2002) points out that "aged, less soluble, and more crystalline forms of Cr(III) (e.g. Cr_2O_3) are much less prone to oxidation." Eary & Rai (1987) show that oxidation to Cr(VI) is rapid in the presence of manganese oxides at pH 3-4.7. Fendorf and Zasoski (1992) studied oxidation of Cr(III) by δ-MnO_2 over a range of concentrations and at pHs from 3 to 5. Although thermodynamics indicated that higher pH and concentrations should favor the reaction, they found that this was not the case, stating "while increases in both pH and ionic strength increased surface charge, these two variables had opposing effects on the oxidation process." Fendorf et al. (1992) found oxidation by Mn-oxides decreased with increasing pH (>4) due to formation of a $Cr(OH)_3$ precipitate on MnO_2 surfaces. Using manganite (γ-MnOOH) as a reactant, Johnson and Xyla (1991) showed that the oxidation rate for Cr(III) was faster than those determined for other Mn-oxides, and that the reaction was "largely independent of pH and ionic strength…" Kozuh et al. (2000) observed oxidation of Cr(III) in soils low in organic-matter content and rich in Mn (VI) oxide. Work by Zhang (2000) found that, in low pH solutions, presence of some organic acids inhibited oxidation induced by light and Fe (III) because of competition from the organic acids with Cr(III) for ·OH radicals. In a study of Cr(III) oxidation by Mn-oxides in the presence of organic ligands (oxylate, citrate, HEDTA) at pH 4 and 10, Tzou et al. (2002) show that although "freshly hydrolyzed Cr(III) could be oxidized by MnO_x at high pH, organic ligands may impede the redox reactions…" , but oxylate "showed low inhibition of Cr(III) oxidation." Saleh et al. (1989) reported slower Cr(III) oxidation rates in sediments where conditions were reversed from anaerobic to aerobic, and slow oxidation in one sample of lake water (pH 7.2). It is clear that, on the basis of the studies cited above, the roles of pH, dissolved and atmospheric oxygen, hydrogen peroxide (H_2O_2), organic acids, sunlight, and iron oxyhydroxides in Cr(III) oxidation are complex. There are relatively few studies that investigate

oxidation of Cr(III) in waste materials, particularly those at the alkaline pHs of COPR materials, but several of these are relevant to the subject of Cr(III) oxidation.

Chuan and Liu (1996) observed that oxidation of Cr(III) species from tannery sludge amendments (high in organic matter) was slower than when pure Cr(III) species are added to soil. Pillay et al. (2003) cited a previous study (Schroeder and Lee, 1975) where oxidation was rapid in alkaline conditions; these relate to their study of oxidation of Cr(III)-bearing slag from stainless steel production. Pillay et al. (2003) found, for ground aged and weathered slags in powder, balls, and pressed pellets, that oxidation proceeded faster in weathered slag samples, and also in powdered samples rather than balls. Smaller particle size also promoted oxidation. A control experiment under N_2, similar to that of James (1994), indicated that "the oxidation reaction proceeds due to the presence of atmospheric oxygen." Furthermore, increasing the level of calcium present enhanced oxidation, as did the presence of atmospheric moisture. Pillay et al. (2003) conclude that, for weathered (decrepitated) slag, more surface area is exposed over time, thus allowing further oxidation, and that "a small fraction of the residual trivalent chromium in alkaline slag is amenable to atmospheric oxidation." It is not clear whether Pillay et al. (2003) measured Mn in the slag materials, so it is not known to what extent, if any, Mn oxides may have been involved in the oxidation attributed to atmospheric oxidation.

James (1994) conducted laboratory studies using COPR soils under various conditions. Interestingly, he found that at pH 8 to 10, neither oxidation nor reduction occurred when soluble Cr(VI) was added to a high-Cr(VI) soil and to a low-Cr(VI) soil. Additional factors such as Mn(II) and lactic acid were significant reductants, however--the former at high pH. Geelhoed et al. (1999) point out that at low pH (below pH 5) and low Cr(III) concentration, oxidation is fairly rapid, but that at pH above 5, Cr(III) precipitates on the Mn-oxide surface, thus restricting the reaction. They also point out that oxidation of Cr(III) by oxygen is "extremely slow" (Geelhoed et al. 1996 - citing Van der Weijden and Reith 1982). James (1994) interpreted results of experiments involving COPR and COPR by-products conducted under air and N_2 to indicate that oxidation of Cr(III) by oxygen does not explain Cr(VI) precipitates, or blooms, that occur on surficial materials and basement walls at and near some COPR sites. Additional experiments by James (1994) indicated some oxidation of Cr(III) added to soils containing low concentrations of Cr(VI), but oxidation of Cr(III) was not apparent in soils with high concentrations of Cr(VI).

Rock et al. (2001) show that, on soils contaminated with COPR, a H_2O_2 leaching solution produced higher concentrations of Cr(VI) than did a solution containing $NaNO_3$ within a 24-hr period. No decrease in Cr(VI) attributable to reduction was noted after H_2O_2 disappeared from the leachate. Rock et al. (2001) point out that, thermodynamically, oxidation of Cr(III) by H_2O_2 is favorable, although the increase in Cr(VI) in leachate does not prove oxidation. They also suggest that a Cr(VI) peroxide complex may have formed. No reduction of Cr(VI) by H_2O_2, which is thermodynamically possible, was observed. Hydrogen peroxide (H_2O_2) has been postulated to form naturally in water as a result of sunlight-induced reactions, and has been measured in both surface-water and ground-water samples exposed to light (Thurman, 1985). Further, Zhang (2000) reported light- and Fe (III)-induced oxidation of Cr(III) in simulated atmospheric waters containing Mn(II) and organic acids. There are no available data from COPR sites to indicate whether or not such reactions take place or are of environmental significance.

Reduction of Hexavalent to Trivalent Chromium

While the charge specifically refers to the oxidation of trivalent chromium to hexavalent chromium, it implicitly includes the reduction of hexavalent chromium to trivalent chromium as well. Hexavalent chromium in soils is reduced by Fe(II) (Buerge and Hug, 1997 and 1999; Seaman, et al., 1999; Fendorf et al., 1997). The Fe(II) may derive from reduction of Fe(III) in hydroxide phases, and this reaction may involve organic matter (Wittbrodt and Palmer, 1996). The experiments of Wittbrodt and Palmer (1996) indicate that Fe(III) may be rapidly reduced by soil humic acid, and the Fe(II) then reduces Cr(VI) or that a ferric chromate complex is reduced by humic acids. They point out that reduction of Cr(VI) is slower at higher pH (their experiments were at pH 2, 4, and 6). Fendorf and Li (1996) determined Cr(VI) reduction rates in solutions containing Fe(II) over a pH range of 6.0-8.0. They found that Fe(II) is an "effective reductant," and they indicate that oxygen would limit Cr(VI) reduction only at pH values >8. Henderson (1994) also points out that reduction of Cr(VI) is slow in ground water at "near-neutral pH values." Reduction of Cr(VI) can take place after adsorption has occurred—Deng and Stone (1996), using experimental solutions with suspended solids, indicate that adsorption is an important condition for the reduction reaction to take place. Eary and Rai (1988) conducted laboratory studies showing that, in experimental solutions, reduction of Cr(VI) to Cr(III) is favored in the presence of Fe(II) salts over a pH range of 2.0-12.0. Solubility of precipitated $Cr_xFe_{1-x})(OH)_3$ limited Cr(III) concentrations in the pH range of 5.0-11.0. Anderson et al. (1994) observed that Cr(VI) reduction in sandy aquifer sediments occurred in the presence of Fe(II)-bearing minerals and increased with decreasing pH. Further, the results of these batch studies suggest that organic compounds, even in small amounts, may influence the availability of Fe(II) by reducing Fe(III). They propose that organic matter, in and of itself, did not reduce the Cr(VI), but that organic matter affects reduction by making more Fe(II) available for reaction. Other researchers have shown that the presence of organic matter increases Cr(VI) reduction (Bartlett & James, 1988; Bartlett & Kimble, 1976); Losi et al., 1994). Wittbrodt and Palmer (1995) report that reduction rates of Cr(VI) in the presence of organic matter is strongly pH dependent, increasing with decreasing pH.   Additionally, some bacteria have been shown to reduce Cr(VI) to Cr(III). Guha (2004) observed this microbiologically-mediated reduction by *Shewanella alga* in a laboratory study. In this study, it was noted that reduction rates decreased significantly in the presence of manganese oxide.

Competing Redox Reactions at COPR Sites

A recent study (Böhm & Fischer 2004) presents the proposition: "The actual Cr(VI) concentration in aerated topsoils is determined by two contrary processes: the Cr(III)-oxidation by Mn oxides and the reduction of Cr(VI) by soil organic matter. It depends on the temporary predominance of one of these reactions…" Bartlett (1991) also states that as site conditions vary, oxidation or reduction will dominate. James (2002) presents a visual model of the relationship between organic matter and manganese (Mn[III,IV] [hydro]oxides) on chromium oxidation, depicted in Figure 6.1. In effect, this seesaw depiction describes the phenomenon described by Böhm & Fischer (2004). The James' papers indicate that pH is a "master variable" for both oxidation and reduction reactions. The point of this illustration is to show that many

variables control the interconversion of the chromium species and that a change in any of them can alter which reaction dominates.

Recognizing that the initial interconversion charge is specific to the COPR sites, the phenomenon of the oxidation of trivalent to hexavalent chromium should be evaluated using the conditions found at COPR sites. The pH regimes found at these sites may vary somewhat, depending upon the proportions of the highly alkaline COPR material to the soils with which it may be mixed. The amount (or presence/absence) of organic matter and Mn-Fe oxides also will vary depending upon the amount and type of soil present in soil/COPR mixtures. If, for example, manganese oxides (Mn(III,IV)) are absent at sites dominated by COPR material, this would preclude the oxidation of Cr(III) to Cr(VI) by this mechanism. Nevertheless, as shown by Pillay et al (2003), atmospheric oxygen can oxidize small amounts of Cr(III) in alkaline slags, and the smaller the particle (with larger surface area) the more likely this reaction will occur. It would appear that, if COPR is subject to vehicular traffic or other disturbances at some sites, that fresh surfaces could be exposed, and that oxidation would occur to a greater extent under such conditions than at sites where COPR is not disturbed and has little contact with the atmosphere. Although the amount of Cr(III) in COPR that could be oxidized over several years may represent a small percentage of the total Cr(III), the mass of Cr(III) present at a site may be sufficiently large that even small percentages oxidized to Cr(VI) could represent a significant environmental hazard. Using data reported in the literature as a guide, an estimate of the mass of Cr(VI) that might be generated at New Jersey sites might be made. Further work is needed to investigate the potential for the oxidation of Cr(III) and the reduction of Cr(VI) in COPR and COPR-soil mixtures. Such investigations will help in determining whether cleanup standards need to be adjusted.

For reduction of Cr(VI) to occur there must be available reductants—organic matter is an important reactant. Researchers studying COPR sites in Scotland conclude that organic matter is capable of reducing Cr(VI) in COPR to Cr(III) (Geelhoed et al., 1999). If materials at COPR sites contain little or no organic matter, however, then there is less likelihood that reduction will take place, as the presence of Fe(III) hydroxides, without something to reduce the iron to Fe(II), apparently is not a sufficient condition. Nevertheless, at sites where COPR is mixed with less alkaline soils containing organic matter and iron hydroxides (or Fe(II)-bearing minerals), reduction of Cr(VI) is likely to occur. Thus, at some COPR sites, conditions may be such that Cr(VI) is reduced to a relatively insoluble Cr(III) solid.

Charge Being Addressed

4. Concentration Effect

Enrichment of concentrated hexavalent chromium has been observed on soils and in structures at the sites. Soluble hexavalent chromium dissolves in groundwater and can move throughout the soil column. The chromium becomes concentrated as the water evaporates. Rainfall events and movement of groundwater levels can change the location of these concentrated evaporative fronts. Can the concentration of chromium in the enrichment areas be anticipated and modeled?

Is there a concentration in the soil that protects against elevated levels of hexavalent chromium from being deposited in this way?

Summary

The phenomenon of enrichment of hexavalent chromium [Cr(VI)] on structures and at the land surface has been documented at the COPR sites in New Jersey. Capillary action is responsible for the movement of the soluble Cr(VI) upward and horizontally. Capillary action is a surface tension phenomena that causes the retention of moisture in the pores of a soil above the water table. Capillary action causes water to move from saturated soils to drier soil against the force of gravity, much like how plants transport liquid from the roots. The height of capillary rise is a function of the pore size and pore size distribution in the soil, which is related to the grain size distribution and density of the soil. In silt loam soils, common at many COPR sites, this rise can reach eight to nine feet above the water table. Theoretically, a rise of up to 15 feet is possible in a loam or silty clay loam soil (Knuteson et al, 1989). In sandy soils, which have larger pore sizes between soil particles, the pull is less, perhaps reaching 1.5 to 2 feet above the water table. Concentration differentials of Cr(VI) have been observed only in areas where the Cr(VI) is very high already. That is, at sites having high concentrations of Cr(VI) in the soil due to the presence of COPR slag, one would expect to see visible blooms in the form of chromium salt precipitates occurring at the land surface and on basement walls and other porous structures. However, there has been no demonstrated chromium enrichment in the form of visible blooms at sites where the Cr(VI) concentrations are lower. Because the blooms can be transient, their formation and disappearance may have gone unnoticed, or the factors involved in bloom formation may not be completely understood. Given the complexity of the factors involved, it is determined that it is difficult at this time to develop a predictive model for this transport mechanism.

The presence of Cr(VI) on small, respirable particles on unpaved surfaces warrants further investigation because such particles can be re-suspended by vehicles and by wind. This phenomenon is described in more detail in Chapter 5 of this report. The generic cleanup numbers are based on conservative estimates of a hypothetical site. Currently, the development of alternative remediation standards (ARS) is allowable by law. These standards can be developed by responsible parties to more accurately model the distribution of chromium on particles specific to their sites. However, the actual numbers generated by this process have been difficult to replicate. It is often mentioned in the literature that chromium adsorbs more to smaller particles than to coarser particles. This mechanism is expected to occur at COPR sites and should be accounted for in the development of both generic standards (which it is) and alternative remediation standards (which is unclear).

This charge was divided into two principal components in order to address the issues associated with the overall phenomenon of the potential enrichment of chromium on small particles and through evaporative increases of concentration on soil surfaces and on structures over time.

Evaporative Enrichment (leading to the precipitation of chromium salts, as "blooms")

For the purposes of this report, evaporative enrichment is defined as the transport of hexavalent chromium dissolved in groundwater or soil solution to surfaces where evaporation can concentrate the solution and possibly cause crystals of hexavalent chromium-bearing minerals to

precipitate. Surface enrichment may, but often may not be, discernable by yellow or yellow-green chromium "blooms", or crystallization of hexavalent chromium salts on the surface of walls or on the waste itself. The phenomenon may occur at the ground surface, on basement floors and walls, and possibly at other locations where soil solution or groundwater seeps to surfaces where evaporation can take place. Chromium salts dissolve in the water and is transported with water until a surface is reached. During dry periods, the water recedes, but the chromium salts remain precipitated on the surface of a concrete basement or surface soil or any other surface where evaporation of water and precipitation of salts can occur.

The evaporative enrichment phenomenon can occur by unsaturated transport of salts by infiltration and percolation, followed by evaporation of water from a surface. This phenomenon is of concern because hexavalent chromium may eventually be transported to a location where it can expose humans to inhalation risks, either by reaching the land surface or by seeping through walls or floors. Such evaporative blooms have been observed in basements of homes built on land where COPR was used as fill and in areas where hexavalent chromium concentrations are quite elevated. It is not known to what extent the phenomenon exists at lower soil chromium concentrations, or if there is a threshold concentration under which it does not occur.

While evaporation may be the most important factor in the appearance of blooms, there are other factors, particularly in soil, that are pertinent, including the type and nature of the material present, the number of available adsorption sites, the pH, the zero-point charge, the redox status, and the presence of organic reductants.

Two processes are of interest: 1) capillary transport of chromium upward from the subsurface to the soil surface; and 2) transport of dissolved chromium through soil and into structures.

1) Capillary Transport of Chromium Upward from the Subsurface to the Soil Surface

Evaporation helps to draw the soil solution upward toward the ground surface by increasing the suction pressure within the soil solution that clings to the solid grains in the porous medium Cr(VI) blooms occur by this mechanism when the depth to the water table is low and less than the thickness of the capillary zone. Data show that blooms become visible on land surfaces where gross contamination of Cr(VI) is dominated by the presence of pure COPR waste. In New Jersey, the net direction of bulk water flow in soil is downward. However, such infiltration downward through the soil column with subsequent groundwater recharge may be inhibited at times in zones where the capillary zone reaches the soil surface.

Visible blooms in areas of significant surface enrichment are typically associated with high hexavalent chromium concentrations. Initially observed in areas known to be disposal sites for pure waste, this surface enrichment on the waste was transient and appeared related to periods of dryness following precipitation events, but it has not been observed at all COPR sites. While these latter sites without visible blooms contain elevated soil chromium levels, the levels are not typically as high as those recorded at the sites where large amounts of pure waste have been deposited. Salts observed at COPR slag and adjacent sites have been confirmed as chromate. These evaporite-like deposits are transient, being readily dissolved by rainfall. When surveyed, elevated chromium concentrations in runoff, groundwater, and river sediments have been

detected proximate to these sites. Field data have confirmed the presence of chromate but have not fully characterized its distribution within the soil profile. The chromate blooms observed at many of the COPR sites occur when hexavalent chromium salts precipitate on the surface of poorly drained soils where shallow groundwater and a capillary fringe permit upward movement and evaporation of soil water containing these soluble chromate salts (James, 1994). This phenomenon has been observed on the ground surface directly above COPR, and on basement walls directly adjacent to COPR deposits (IT Corp., 1992 and 1995). The chromate blooms have not been observed at every site where COPR is found at the surface. Nor have blooms been seen across the entirety of those COPR sites where blooms have been occasionally observed. The blooms can appear during dry periods, when evaporation of soil water occurs at the soil surface, and the blooms can disappear when rainwater dissolves the salts again (James, 1994). Despite the recurrent nature of the blooms in some locations, some of the specific conditions required to create such blooms remain to be identified. Also, field measurements are needed to learn whether the absence of a visible bloom is sufficient to rule out evaporative enrichment. Thus, knowledge of Cr(VI) levels in soils might not be sufficient to predict blooms at COPR sites, except at highly contaminated sites where visible blooms have been recorded regularly. A variety of physical and chemical conditions contribute to bloom formation, such as total Cr(VI) and water soluble Cr(VI) concentrations, pH, and wetting/drying cycles.

2) Solute Transport of Chromium through Soil and into Structures

The presence of Cr(VI) inside buildings resulting from unsaturated or saturated transport can lead to human exposure. Water can be a vehicle to transport soluble Cr(VI) into interior living or working spaces. In this scenario, water contaminated with Cr(VI) moves through concrete slabs or cinder block indoors and deposits the soluble chromium through the evaporation of the water. Over time, the deposited Cr(VI) becomes incorporated into basement dust and is suspended by various activities.

During remedial investigations at COPR sites, the presence of chromate salts on the interior wall surfaces was observed as green or yellow precipitates. This led to a conscious effort to visually inspect all interior and exterior building surfaces (and sample when appropriate) constructed on or near COPR sites for the presence of more blooms or for conditions that would favor the development of blooms. After inspection of structures at numerous sites, it was determined that the occurrence of visible chromate salts on interior wall surfaces was associated with very high hexavalent chromium concentrations in surrounding soil in direct contact with the structures. Blooms were not observed in areas where these conditions were not met. Analytical tests were not completed, so it is not known whether Cr(VI) salt deposits were present at concentrations that would not cause a visible bloom. The most probable mechanism was determined to be hexavalent chromium contaminated water seeping horizontally or "wicking" upward through the concrete or cinder block or mortar joints. Evaporation promoted the seepage through the concrete. Subsequent evaporation and crystallization then resulted in the observed salt formation. Review of a subset of the Hudson County Chromium Sites (those of Tierra Solutions, Inc.) illustrates the observations (Brown and Caldwell, 1999, 2001a, and 2001b). Of the 40 sites being addressed by Tierra, four sites (Sites 41, 47, 58, and 209) exhibit chromate salt formation on interior walls. Interim remedial measures have been taken at these sites, which include the use of epoxy coverings to isolate salts from human contact, as well as mandated routine

inspection and testing. The experience has been that, extant physical damage to the epoxy coverings, these measures have been protective. However, despite years of inspection, new areas of chromate salt formation have not been observed and the known areas show neither significant migration nor expansion nor any change in location of chromate salt formation. This indicates certain stability in the occurrence of these visible salt formations that perhaps equilibrium is reached over time.

Examination of the cause of the chromate salt formations suggests an association with nearby high hexavalent chromium concentrations. Peak soil boring Cr(VI) concentrations of 6,940; 8,200; 1,620 (with 4,130 below); and 5,300 mg/kg were found at sites where evaporite salts were observed in basements. While elevated, these concentrations do not necessarily represent the maximum seen during the remedial investigations. Clearly, a source of chromate salts at significant concentration is one factor that can be used to predict salt deposition in basements, but it seems proximity to the contamination is also important. On a general level, the expected reductive and adsorptive capacity of the soil may affect the horizontal distance from the source where this phenomenon can occur, explaining the absence of the phenomenon in areas where chromium concentrations are not elevated. However, it does suggest that additional factors may be involved in the observed infrequency of the salt formation.

Weng et al. (2002) have explored the possibility of developing a predictive model to estimate the potential for hexavalent chromium to form salts on interior walls of residential structures. They determined that the factors are too complicated to model. The number of variables involved and the uncertainty surrounding them precluded the development of an adequate transport model for these researchers. Therefore it is recommended that the current SRWMP empirical approach to evaluate this potential concern during the remediation of each site is the most practical approach at this time and should be continued in conjunction with any model that may eventually be developed.

Particle Enrichment

For the purposes of this report, particle enrichment has been defined as the preferential adsorption of hexavalent chromium on smaller particle sizes such as clay-sized particles. This can occur at the surface of the soil, which is of concern here, or at depth through the soil column, which is a factor in chromium transport to groundwater. The issue of concern here is that vehicular activity on unpaved surfaces of COPR sites will result in the suspension of airborne particulates (small particles with sorbed hexavalent chromium) from the surface of the soil. If the chromium is associated with the surface particles, it will also be associated with the airborne particulates suspended from that surface.

The phenomenon when it occurs on the land surface is important because the inhalation risk-based soil clean-up criterion for chromium is determined by modeling the risk from respirable particles less than 10 microns in size. There are two types of models used to calculate soil cleanup levels. The first model predicts emission rates of particulates from truck traffic and wind-blown dust. The second is used to describe the movement of this particulate through the air and predict air concentrations at designated points at and around the site. These predicted concentrations are then used to back-calculate to the soil concentration that would result in the

one in a million cancer risk level for a specific contaminant, Cr(VI), and is compared against the soil chromium concentration in bulk soil samples collected at the top 0-6 inches. Thus, there is concern that the current methodology by which bulk sampling techniques are compared to the inhalation risk level may underestimate the risk because the sampling method does not distinguish among the different sized particles. Adsorption and other mechanisms that distribute mass on particle surfaces raise concerns that small particles may contain more chromium per mass of particles than the coarser soil particles. Techniques for separating the smaller particles are not fully developed for routine uses.

Surface area per unit mass of soil is greatest for the smallest-sized soil particles. For instance, a cobblestone could have a surface area of one square meter. If the cobble is repeatedly struck with a sledgehammer, it could be broken into possibly 100,000 individual particles while still containing the same mass of the intact cobble. Collectively these smaller particles would have a greater surface area than the initial one square meter of the intact cobble. Therefore, the surface area per unit mass is inordinately greater for the pulverized rock than for the intact cobblestone. Adsorption of contaminants onto these particles is a surface phenomenon in which a chemical species adheres to the soil interface. The larger the surface area the higher the opportunity for adsorption. The clay-sized fraction represents a significant component of soils for adsorption because they are found in layers throughout the soil column and their small size provides abundant surface area for adsorption of chromium (or other contaminant).

The smaller the soil particle or sediment grain, the larger is its surface area relative to its volume. The surface area of a gram of fine colloidal clay is about a thousand times that of a gram of medium sand. Thus, the capacity for adsorption is much greater for small soil particles than it is for large particles (Brady, 1974 and 1996). Adriano (1986), in summarizing studies of trace elements and their relation to particle-size fractions and soil horizons, reports that Korte et al. (1976) show a strong correlation between the capacity of soils for cations, the amount of clay, and the surface area. The correlation for anions is stronger for free iron hydroxides than it is for clays or surface area; nevertheless, soils of clay or silty clay texture, with a percentage of clay over 50%, and surface areas of more than 50 cm^2/g, are shown to have a high capacity for oxyanions such as dichromate ($Cr_2O_7^{2-}$). The correlation of oxyanions with iron hydroxides is expected, as the anions are most likely to be adsorbed to positively charged surfaces such as iron hydroxides (with a zero point of charge of about 8.5). Oxyanions such as chromate have less affinity for clays, which generally have negatively charged surfaces except when highly protonated at low pH. Iron is contained in significant concentrations in COPR sites, and amounts of Fe_2O_3 have been measured at 51% of total soil sample at these sites (Gafafer, 1955 as reported by Kitsa et al. 1992).

Adriano (1986) describes the work of Connor et al. (1957) who found that concentrations of chromium and other trace elements were higher in B or C horizons (which typically contain illuviated small particles) than in A horizons, and that the clay fraction contained most of the trace elements. Because almost all, if not all, of the sites in Hudson County represent disturbed soils, illuviation and concentration of material in B and C horizons is difficult to define. The soils at and near COPR sites in Hudson County undoubtedly have been disturbed. However, natural soils or sediments did exist at these locations before the disturbance for construction and use of COPR as fill. The clays and iron and aluminum oxyhydroxides continue to be present in

the soils, and typically retain the bulk of the trace metals, especially in areas where COPR is mixed with the original soils. The clay-size particles reported by Connor et al. (1957) happened to be in B and C horizons (which is where one would expect them to accumulate in undisturbed soils). Many trace elements, including chromium, tend to be adsorbed preferentially to small soil particles whether those particles are in well-defined soil horizons or whether the horizons have been disturbed.

Laboratory and field studies have demonstrated that adsorption of chromium occurs in soil and that it occurs more on smaller particles than on coarse particles. However, particle size is not the only factor influencing the adsorption and therefore the enrichment of chromium. Adsorption is strongly controlled by pH, the type of material, number of available adsorption sites, redox status, presence of organic reductants, and other environmental factors that control the fate and transport of hexavalent chromium (USEPA 1999, Farmer, et al. 2002, Weng, et al 2002, Weng, et al. 1994, Loyaux-Lawniczak et al. 2001, Pettine, et al. 2002, Grove and Stollenwerk 1985, Gaberell, et al. 2003, Anderson, et al. 1994, Deng and Stone 1996, Wittbrodt and Palmer 1995, Wittbrodt and Palmer 1996, Buerge and Hug 1997, Buerge and Hug 1998, Buerge and Hug 1999, Seaman, et al. 1999, Henderson 1994, Jardine, et al. 1999, Kozuh, et al. 2000, Lee and Batchelor 2003, Davis and Olsen 1995, Brigatti, et al. 2000, Tokunaga, et al. 2001, and Palmer and Puls 1994).

Anderson et al. (1994) found that reduction of hexavalent chromium increased as the amount of fine particles increased, which was attributed to the increase in the surface area of the fines. The relationship between adsorption of and reduction of chromium is a complex and interrelated process that is not fully understood though many studies report that the same factors controlling adsorption of chromium also control reduction. Based on Deng and Stone's 1996 work, where they indicate that adsorption is an important condition for the reduction reaction to take place, it may be that less adsorption at higher pH has an effect on the reduction rate. While there are no studies directly measuring this relationship, the data are suggestive. It seems that in COPR-affected soils with pH less than about 8.5, adsorption of Cr(VI) can occur. At pH levels above 8.5 (especially at COPR sites where the pH of contaminated soils is greater than and the pH of the pure waste ranges from 10 to 12), adsorption may be less significant. It would appear that at the pH and Eh conditions of soils at COPR sites, hexavalent chromium reduction and adsorption may occur and that the two processes may be related. Ramos, et al. (1994) concluded that the adsorption of hexavalent chromium onto activated carbon was greatly dependent on pH and, in fact, was diminished about 17 times by increasing the pH from 6 to 10. Because of the wide range of soil characteristics and various forms by which metals can be added to soil, evaluating the extent of metal retention by a soil is site/soil/waste specific. Changes in the soil environment over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes also may enhance chromium mobility and reduce chromium adsorption.

Adsorption mechanisms specific to COPR material or COPR-soil mixtures would have a significant impact on hexavalent chromium levels on all sizes of particles (especially at COPR sites where the contaminated soils are greater than pH 7 and the pure waste is 10 to 12). The influence of other factors may in part explain discrepancies between adsorption predicted on a surface area only basis and the reported data that are specifically COPR related. In the case of

pure COPR materials, if Cr(VI) is distributed throughout the COPR slag, it is possible that concentrations in various particle sizes of slag may not be substantially different. But in contaminated soils, where Cr(VI) leached from slag may have adsorbed to soil particles, the smaller particles could be expected to contain higher concentrations of Cr(VI) than large particles because of the smaller particles' larger specific surface area.

Not only does pH play a role in determining the charge distributions on solid surfaces to which chromium species can adsorb, it is a critical determinant of the chromium species that are present in an aqueous medium. Cr (VI), dominant under oxidizing conditions, is protonated at pH less than 7, existing as $HCrO_4^-$. At higher pH, Cr (VI) is present as CrO_4^{2-}. The Cr (VI) species do not generally form complexes with inorganic or organic ligands. Reducing conditions favor formation of Cr (III) compounds, which can be present as cations (successively Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^+$) up to about pH 8.4. The neutral species $Cr(OH)_3^0$ is then dominant to about pH 10, and the anion $Cr(OH)_4^-$ dominates at higher pH (Calder, 1988). Because Cr (III) species are cationic over a large pH range whereas Cr (VI) species are anionic, differences have been noted in adsorption behavior for Cr (III) and Cr (V) to clays and iron hydroxides with their differing surface charges. Zayed and Terry (2003) postulate that the adsorption of Cr(III) to soil clay minerals increases with increasing pH. When the pH increases to levels above 8.5, adsorption of Cr(VI) is not observed. They cite the work of Griffing et al. (1977) who state that Cr(III) is adsorbed 30-300 fold more strongly to soil clay minerals than Cr(VI). Richard and Bourg (1991) reported a similar pattern.

Adsorption of Cr (VI), in particular, has some relevance to understanding the leachability and mobility of Cr (VI) derived from COPR wastes. Leaching experiments conducted by Weng et al. (2002), attempted to characterize the Cr(VI) leaching process in soils enriched with COPR. The leaching experiments were performed on crushed samples, with particles less than 1 mm, and having an average size of 250 microns. Weng et al. (2002) concluded that chromate can be readily leached from the surface of the COPR-soil particles and that the amount leached increased with increases in temperature. Results from this study therefore imply that release of Cr(VI) is important in these areas and that transport downward to groundwater is a significant pathway of concern (see section on Impact to Groundwater for a more detailed discussion of Cr(VI) mobility). Preferential adsorption of Cr (VI) on small particles has been shown to occur at low to slightly alkaline pH. At higher pH, the Cr(VI) tends to be soluble and would tend to follow soil water rather than to sorb to particles, regardless of the particle size. At COPR sites, it is proposed that there is a steady dissolution of hexavalent chromium from the slag to surrounding soil. Adsorption may also occur to some extent. To date, there has been no evidence presented in the literature showing that the adsorption of hexavalent chromium at sites dominated by COPR waste is a significant issue. However, adsorption may occur to varying extents as sites where COPR is present in smaller amounts, mixed with soils of less alkaline pH.

Cowherd et al. 1985 adopted the bulk soil concentration as the best available concentration estimate for the suspended particles, while acknowledging that concentrations on the finest particles may be enriched:

"Contaminants in particulate form may be present either as discrete solid particles or adsorbed onto soil or other surface aggregate materials. This depends on the physical and chemical

interaction between the contaminant species and the surface aggregate. For adsorbed contaminants, there is usually an enrichment of contamination in the finer particle sizes because of larger surface-to-volume ratio. However, in the absence of data on the contamination level of PM_{10} particles in the surface material, it will be assumed that the level of contamination ... in the respirable particulate emissions matches that measured in the bulk surface material."

Falerios, et al. (1992) provided mean ratios of respirable hexavalent chromium and total suspended particulate hexavalent chromium. The respirable fraction was defined as less than 10 micron and the total suspended particulate fraction was defined as less than 75 micron. The average concentrations for these sites show that the ratio of respirable particle Cr to total suspended particle Cr is 0.6.

A report describing chrome fractionation studies was submitted by PPG Industries to the Department in 1995 as part of the Remedial Investigation phase of a site in Hudson County (ICF Kaiser Engineers, 1993). The final report addresses NJDEP concerns about whether hexavalent chromium concentrations differed between the bulk samples and the fractions. While the authors report that "…bulk hexavalent chromium concentrations are conservative when used to estimate the hexavalent chromium concentrations in less than 75 micron and less than 10 micron size fractions," a statistical evaluation of the data by a NJDEP statistician (Korn, 2004, personal communication) indicates that this statement may not be complete. The authors cite this report as justification to discontinue soil fractionation and particle size analysis for hexavalent chromium. However, the data seem to be equivocal, at best. In the report, the argument is made that even though there is no evidence that the bulk Cr(VI) concentration is greater than Cr(VI) on smaller fractions, the concentrations are equivalent. This kind of testing has low power, so it should not be considered as strong evidence of equivalence. In summary, the report does not present evidence that Cr(VI) concentrations in bulk soil samples is higher or equal to Cr(VI) concentrations on smaller particles.

One of the few academic studies that have directly measured chromium levels on soils by particle size at New Jersey chromium sites was conducted by Kitsa et al. (1992). In this study, enrichment of chromium and other metals on particles between 10 and 30 microns was observed. Chromium concentrations on particles less than $PM_{2.5}$ and greater than PM_{30} were lower. Particles less than PM_{10} (10 microns) are considered to represent the thoracic fraction, and particles less than $PM_{2.5}$ (2.5 microns) are considered to represent the respirable fraction. Particles less than PM_{30} (30 microns) represent the inspirable fraction. The $PM_{2.5}$ particles inhaled beyond the nasal passageways are not rejected. Rather, these particles are able to reach the lung. Therefore, the exposure to humans through these respirable particles is of particular interest. In experiments using a resuspension chamber and x-ray fluorescence analysis, the investigators report some interesting results. While chromium levels in areas of visible blooms showed increasing chromium concentrations with decreasing particle size (to $PM_{2.5}$), soils from contaminated sites but not in visible bloom areas and soils from background sites demonstrated an opposite trend. That is, enrichment of chromium on small particles seemed to occur when chromium levels were very high (above 11,000 ppm in bloom areas) but was not observed when total chromium levels were lower. Mean total chromium concentrations of 12,885; 8,591; and 7,941 mg/kg were measured on particle size fractions of between 10 and 30 microns, between 2.5 and 10 microns, and less than 2.5 microns, respectively using x-ray fluorescence analysis of

filters obtained from resuspension chamber experiments. Data taken from the study tables showing samples collected in 1991 are shown in Figure 6.2. It would appear that in a soil system inundated with chromium, adsorption sites on the smaller particles become filled with chromium; whereas in less contaminated soils, a more homogeneous distribution among particle sizes occurs. The researchers conclude that: "Thus it appears that exposure to high concentrations of contaminated dust occurs primarily during resuspension conditions at sites with visible hexavalent chromium crystals." Interestingly, the percentage of hexavalent chromium decreased with particle size: hexavalent chromium was 60%, 50% and 20% of the total extractable chromium found in the PM_{30}, PM_{10} and $PM_{2.5}$ size fractions, respectively. If the particles of all sizes are composed of chromium bearing minerals, it might be expected that concentrations would be much the same from one size class to another. Examples of non-uniform concentrations could include fine, unattached crystals of evaporite from chromate solutions or chromium distributed somewhat uniformly over the surface area of the particles. Enrichment factors were calculated as part of the study. They show that the enrichment in total chromium at COPR sites are high when compared to rural soil. However, the enrichment factors are lowest for $PM_{2.5}$ particles (65) than for the PM_{10} particles (352) or for the PM_{30} particles (452). One of the conclusions of the report is: "Thus, it appears that exposure to high concentrations of contaminated dust occurs primarily during resuspension conditions at sites with visible hexavalent chromium crystals." Later, they add, "…hexavalent chromium in crystal or 'bloom'-laden soil is bioavailable in size fractions that are of concern for deposition in the respiratory system."

Application of how the results from the Kitsa et al. (1992) study is used in calculating the air dust exposure model is discussed further in the Air Transport section of this report (Chapter 5).

Assuming that there is a consistent enrichment of smaller particles in relation to the bulk soil concentration, and assuming that the enrichment is significant, how might the generic soil clean-up criteria for this pathway change? This question was posed to the air transport group. Using those assumptions, a weighted average method could be used to account for the higher concentration, and would result in a somewhat lower allowable concentration of Cr(VI) in soil. How much lower depends on the degree of Cr(VI) concentration on the particles. One sample calculation suggests that an order of magnitude increase in Cr(VI) on the small particles (PM 2.5) would lower the allowable soil concentration by about 25%, bringing the generic number from the proposed 20 ppm to about 15 ppm. Although this difference is not large, particularly given the conservative nature of the models and the conservative toxicity data employed to calculate the standards, the issue remains significant. The Department should continue investigating, through studies and through ARS petitions, the possibility that smaller particles contain higher concentrations of Cr(VI) than bulk soil concentrations and, if appropriate, consider developing an enrichment model to account for the difference.

The literature combined with empirical data submitted to the Department by responsible parties specifically from COPR sites in the state show no consistent enrichment of hexavalent chromium on smaller particle sizes nor do they show consistent equal concentrations of chromium on bulk and fractionated samples. While some level of enrichment may occur, the factor has not been quantified to date.

Recommendations

1. Nature of COPR

Research:

- The Department should consider developing a research project using x-ray based technologies and scanning electron microscopy to better characterize the mineralogy of COPR at the New Jersey COPR sites. It has not been established definitively that the COPR sites in New Jersey are identical to those in Scotland, where some detailed mineralogical studies have been conducted. A small project to better investigate the nature of the minerals present at New Jersey COPR sites would enhance the Department's understanding of the fate and transport of chromium at these sites.

2. Transport to Groundwater

Programmatic:

- Recommend that the Department consider defining COPR waste material and soil with larger amounts of COPR waste material as a continuing source of contamination to groundwater that will require remediation in accordance with the Department's Technical Requirements for Site Remediation (N.J.A.C. 7:26E).

Research:

- Criteria for separating COPR waste from chromium-contaminated soil.

- Exploration of the applicability of the Synthetic Precipitation Leaching Procedure at COPR waste sites.

- Investigation of the reduction capacity of meadow mats at COPR waste sites.

- Investigation of the reduction capacity of aquifer material at COPR waste sites.

- Investigation of chromium adsorption-desorption process on chromium-contaminated soil (not COPR material) in the vicinity of the waste sites. While chromium adsorption-desorption studies have been conducted on NJ soils, the soils were not from COPR sites. It is important to perform similar studies using soils in or near COPR waste sites.

- Recommend that the Department consider defining COPR waste material and soil with larger amounts of COPR waste material as a continuing source of contamination to groundwater that will require remediation in accordance with the Department's Technical Requirements for Site Remediation (N.J.A.C. 7:26E).

- The Department should begin work immediately to differentiate pure COPR slag waste from COPR-soil mixtures. Such differentiation can be based on chemical characteristics such as pH and mineralogy.

3. Interconversion

Research:

Because the conditions at COPR sites are variable, oxidation of trivalent chromium to the hexavalent form may occur only sparingly, but at some sites the mass generated over time may become environmentally significant. If the pH of soils at some sites is sufficiently low and the soils contain suitable reductants, Cr(VI) in COPR may be reduced. It is believed that proposed clean-up standards for chromium will be protective of human health; however it is recommended that oxidation rates of Cr(III) in COPR be further investigated to determine under what circumstances, if any, the production of Cr(VI) becomes environmentally significant. The determination of Cr(III)-bearing phases in COPR, such as brownmillerite, would be useful, as these may undergo oxidation at a rate that differs from that of chromite.

4. Concentration Effect

Programmatic:

- The Department should continue to monitor structures at COPR sites for the appearance of salts. It is especially important to maintain observations in areas where barriers have been installed to ensure that the salts are not regenerating. Where appropriate, evaluations should include analytical testing in addition to visible assessments.

- The Department should continue to address in a conservative way the inhalation exposure route for hexavalent chromium by recommending the use of its generic model (as described in Chapter 5).

- The approval of an alternative remediation standard should be contingent upon the responsible party conducting site-specific studies in accordance with departmental guidelines. Submissions that do not follow the guidelines should be rejected. Those that do should undergo a rigorous review with a transparent and formal approval process. Any alternative remediation standard developed to address the inhalation exposure route needs to be formally incorporated in to the case records and made available for replication. As described, the sampling and analytical capabilities for determining Cr(VI) concentration on very small particles ($PM_{2.5}$) are not fully developed or available commercially. These methods are still being developed. But there are steps that can be taken to ensure that alternative remediation standards are developed accurately:

  - when a responsible party seeks to develop an alternative remediation standard for inhalation, a complete analysis of Cr(VI) by particle size should be developed, submitted and formally approved by the Department. Such an analysis should

include experiments in a resuspension chamber and use analytical methods consistent with those described in Chapter 3 of this report.
- when investigating and describing a site in relation to the inhalation exposure route, the responsible party should include analysis of the following when determining the presence of particles at the site:
  - wind direction relative to the location of any air samplers and relative to vehicular activity. Samples should be collected downwind of vehicle traffic.
  - time of day of sample collection. Samples should be collected during the normal 8-hour work day.
  - soil sample averaging.

Research

- The Department should consolidate information from its site remediation files on investigations where residential structures are near COPR or COPR-soil mixtures have been studied. Existing data describing the occurrence of Cr(VI) salt formation in basements or other structures is available in the case files. A report consolidating the investigations should be written, published and made publicly available. In instances where data are not available, the Department should initiate studies to collect it. The information should include both analytical as well as visible evaluations of the structures.

- To address the question of whether or not vadose zone transport can cause blooms at low soil chromium concentrations, it is recommended that a study be conducted to investigate the potential occurrence of surface enrichment due to capillary transport of hexavalent chromium. Theoretically, enrichment on surfaces can occur at any Cr(VI) concentration, but it is now known definitively whether or not there is a threshold concentration. Specifically, COPR material and COPR-soil mixtures containing various Cr(VI) concentrations should be studied for potential evaporative enrichment via capillary action toward the goal of determining whether there is a threshold concentration in soil where evaporative enrichment via capillary action does or does not occur. It is especially important to evaluate the possibility of capillary transport at sites so that the Department is better able to evaluate the effectiveness of remedial strategies.

- Offsite migration and delineation of chromium contaminated groundwater from COPR sites should account for the vertical and spatial variability of urban soils. Construction activities (compaction, filling and scraping) may cause changes in the soil profile. These disturbances can influence water movement and retention. The dissolved chromium may migrate offsite and concentrate on surface soils, concrete foundations or any other surface that may be susceptible to capillary action. Currently, delineations are conducted at sites for Cr(VI) until levels reach the drinking water standard of 100 μg/L. It would be useful to investigate the transport of Cr(VI) in groundwater where levels are below this number in order to better understand the ultimate fate and transport of dissolved Cr(VI) in groundwater.

- Information in the published literature (Kitsa et al., 1992 and Falerios et al., 1992) and site data (PPG) present limited data on enrichment of Cr(VI) on smaller soil particles. The

mineralogy of the small soil particles is not known. Research is recommended to clarify whether particle size enrichment is or is not of concern due to the limited data available to address this issue. Systematic, specific research is needed to definitely determine levels of hexavalent chromium on smaller particle in bloom areas, chromium-contaminated areas, and background areas. The mineralogy of small particles in chromium-contaminated areas needs to be determined. The design of the study should be determined by an appropriate group of people from the Department and unbiased external researchers with expertise in this research area. The study should include sample sites from several COPR sites in New Jersey. The Kitsa et al. (1992) study is the only one that approaches this need, but it is dated and limited. The work by Falerios et al. (1992) does not demonstrate that that more chromium is present on the smaller particles. The data are equivocal. Therefore, it appears that further investigation of this matter, as a human health issue, is warranted. A larger and more current investigation than the two described here could illuminate the issue for the state and better inform the soil standard setting process. At the very least, measurements of Cr(VI) on small soil and bloom particles, as well as the routine measurements on bulk samples, could be considered as an important step in assessing human health risks from COPR. Mineralogical characterizations should be completed on samples used in experiments. It might be helpful to compare the concentrations resulting from such a study with those collected from a deep soil core for variation. Several sites plus a control site would need to be included in the study.

- Development of routine methods for particle size analysis for particle size ranges less than PM 10 should be supported.

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